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Study on the photoreaction of 1-(2-chlorobenzoyl) -3-(4-chlorophenyl) urea in methanol

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Abstract— A photoreaction of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) in methanol was studied. Rate constants of its reactions, which are found both of the first order, in methanol solution saturated with N_2 or O_2 upon irradiation with xenon lamp, are determined to be 0.118 and 0.129 h^{-1}, respectively. Its half life changes from 5.37 to 4.42 h when the light intensity is changed from 0.50 to 0.62 cal/cm^2. min. The main photoproducts identified are 2-chloro-benzamide, N-phenyl methylcarbamate, N-(4-chlorophenyl) methylcarbamate, 4-chlorophenyl urea and others. Meanwhile, the mechanism of the photochemical reaction of this compound in methanol was discussed.

Keywords: 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea, CCU; photoreaction; products; methanol; mechanism.

INTRODUCTION

Some papers regarding photobehavior of phenyl urea insecticides were reported (Mazzochi, 1972; Crosby, 1969). In typical halogenated phenyl ureas like DFB and PH6038, there are two alive radicals-amide bond and halogen, so their photoreactions are very interesting, as described by Ruzo (Ruzo, 1974) and Metcalf (Metcalf, 1975). We have reported some studies on photoreaction of 1-2-(chlorobenzoyl)-3-(4-chlorophenyl)urea [CCU] in simulated atmosphere, however, its photoreaction in solution has not been mentioned up to now.

Since the solubility of CCU in water is very low, some additional auxiliary solvents should be required in preparing its aqueous solution. Methanol is one of the best selections as the auxiliary solvent, because the solubility of CCU in it is very high. So the effect of methanol to the photoreaction of CCU should be manifested before starting the research of CCU in water. On the other hand, the study on the photoreaction of CCU with methanol can supply some hints to postulate the photoreaction of CCU with other organics. The study on the kinetics and reaction products of CCU photoreaction in methanol is presented in this paper.

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EXPERIMENTAL

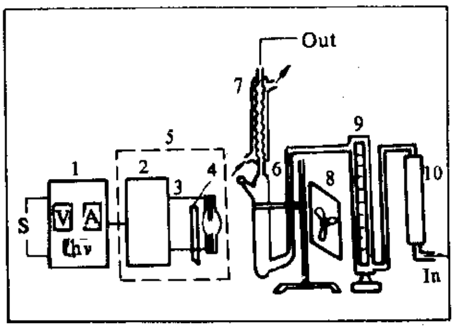
Reagents

CCU, was produced by Tonghua Factory of Insecticides (Jilin Province). After recrystallization with toluene for three times, its purity is about 98%. Methanol was from Beijing Chemical Factory and redistilled before use. Both 2-chlorobenzamide and 4-chlorophenyl urea samples were supplied by Wuhan Institute of Hydrobiology, Chinese Academy of Sciences, while Chlorobenzenes were from USEPA.

Instruments

Shimadzu LC-5A HPLC equipped with SPD-1 detector; XQ-200w xenon lamp with XQ150-500 D. C. power from Shanghai Lightening Device Factory; selfmade quartz reaction chambers. 75L-III accumulative photoradiometer from Tianjin Third Analytical Instrument Factory. Finnigan MAT-4510 GC/MS.

The reaction equipment is shown in Fig. 1.



1. D.C. power supply 2. Trigger
3. Reflector 4. Xenon lamp 5. Lamp box
6. Photoreaction chamber 7. Condenser
8. Cooling fan 9. Flowmeter
10. Purifier of carrier gas

Fig. 1 Scheme of photoreaction equipment (Liu, 1990)

Experimental method

1. HPLC analysis condition

HPLC was used to determine the concentration of CCU in the aliquot samples taken out at previously set time intervals from the reaction chamber during the process of experiment. The analytical conditions were: HPLC column, 250×4.6 mm Zorbax C_8; mobile phase, CH_3OH-H_2O (90:10 v/v), at flow rate 1 ml/min, detector: UV-254 nm.

2. Photoreaction

50 ml methanol solution of about 50 ppm CCU was added into the reaction chamber (Fig. 1), and nitrogen or oxygen was passed through the solution at 40 ml/min, to keep the solution saturated with either of them. The temperature of the chamber was controlled at 25±2°C, and the light intensity was 0.50 cal/cm^2. min. The variation of concentration with time was followed by taking sample for every fixed time and analyzing with HPLC.

Meanwhile, the variation of concentration with time in dark condition was also studied for comparison.

3. Effect of light intensity on the photoreaction of CCU

By changing the distance of reaction chamber from the light source (Fig.1), the light intensity at the place where the chamber was located was varied. The photoreaction kinetics and the photoproducts of CCU in methanol with different light intensities were studied to assure the effect of light intensity to the photoreaction of CCU.

4. Identification of the photoproducts

(1) Separation and identification with HPLC

The HPLC conditions were: HPLC column, 250×4.6 mm Zorbax C_8; mobil phase, CH_3OH-H_2O (70:30, v/v); flow rate at 0.4 ml/min; detector, UV-254 nm.

The retention time and UV absorption spectra of the photoproducts were compared with those of the standard compounds under the same HPLC condition to identify the photoproducts.

(2) Identification with GC-MS

GC-MS conditions were, for GC system, column: SE54, 30m × 0.22 mm i.d., column temperatures were programmed from 60°C to 220°C at 4°C/min, and from 220°C to 300°C at 10°C/min; system: EI, 70eV; ion current at 270 μA; mass scan range: 33–500 amμ; scan for MS speed; 30/min; ionization temperature: 300°C.

RESULTS AND DISCUSSION

Photoreaction kinetics

Photoreaction results of CCU in methanol saturated with nitrogen and oxygen are shown in Fig.2.

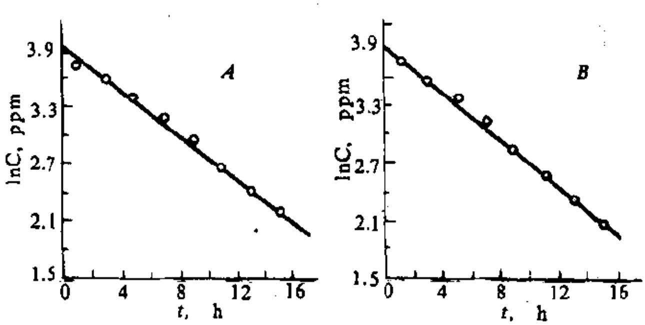


Fig.2 Photoreaction kinetic curves of CCU in methanol

A: nitrogen *B*: oxygen

Photoreactions in both conditions are of the first order. The photoreaction equations are:

under nitrogen: $\ln 1/c = -3.98 + 0.118\ t,\quad r = 0.997;$

under oxygen: $\ln 1/c = -3.99 + 0.129\ t,\quad r = 0.998.$

Here, t is photoreaction time (h), c is the concentration of CCU (ppm) at time t, r is correlation coefficient.

The photoreaction half-lives of CCU in methanol saturated with nitrogen or oxygen were 5.87 and 5.37 hours, respectively. However, statistical verification of the experiment results indicates that there is no significant difference between the reaction rate in both conditions.

In the dark parallel experiment, the concentration of CCU had no variation in 15 hours. This result indicates that the CCU is comparatively stable in methanol without light irradiation, and the variation of concentration of CCU under light irradiation is due to the photoreaction.

Effect of light intensity to the photoreaction

1. Effect to the kinetic of photoreaction

The photoreaction kinetic curves of CCU under oxygen in different light intensity are shown as in Fig.3. The linear equations are:

A: $\ln 1/c = -3.99 + 0.129t,\quad r = 0.998;$

B: $\ln 1/c = -4.04 + 0.157t,\quad r = 0.997.$

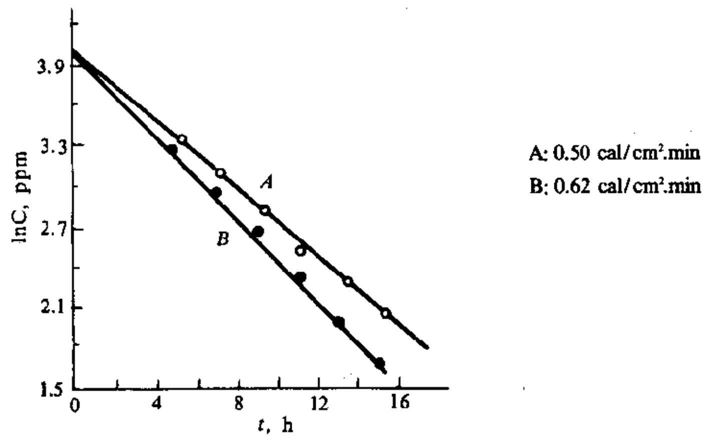


Fig.3 Photoreaction kinetic curves of CCU with different light intensities

The half-lives of CCU are 5.37 and 4.42 hours when the light intensity is 0.50 or 0.62 $cal/cm^2.min$, respectively. The photoreaction rate is proportional to the light intensity. Under the experimental conditions, the difference in light intensity did not effect the orders of photoreaction, i.e. the photoreactions in both cases are the same of the first order.

2. Effect to the photoproducts

The HPLC chromatograms of photoproducts in different light intensity are shown in Fig.4.

The change of light intensity has some effect on the relative proportion of photoproducts, but exerts no effect upon the identities of photoproducts.

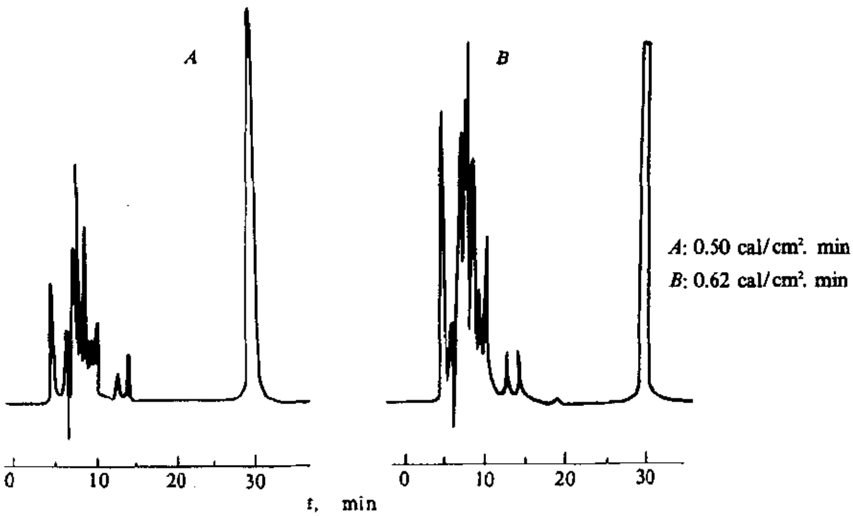


Fig.4 HPLC chromatograms of photoreaction products of CCU in different light intensities

The photoproducts of CCU in methanol

When the methanol solution of CCU at concentration of 50 ppm, saturated with nitrogen or oxygen, was irradiated with xenon lamp, the colour of the solution changed from colourless to yellow and became deeper with the time.

1. Identification with HPLC

The HPLC chromatograms of photoproducts of CCU in methanol saturated with nitrogen and oxygen are shown in Fig. 5, and the HPLC chromatograms of standard substances are shown in Fig.6.

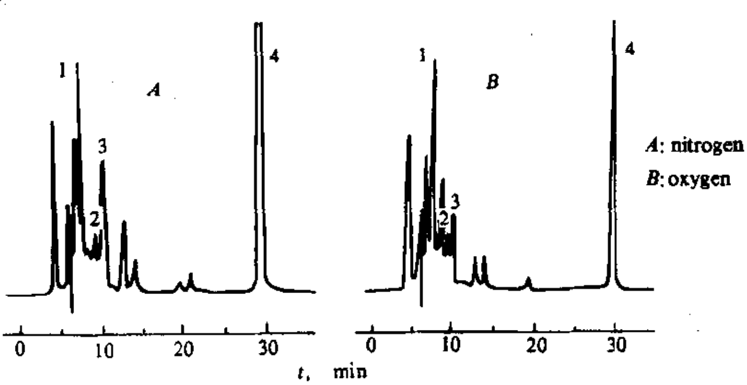


Fig.5 HPLC chromatograms of photoproducts of CCU in methanol

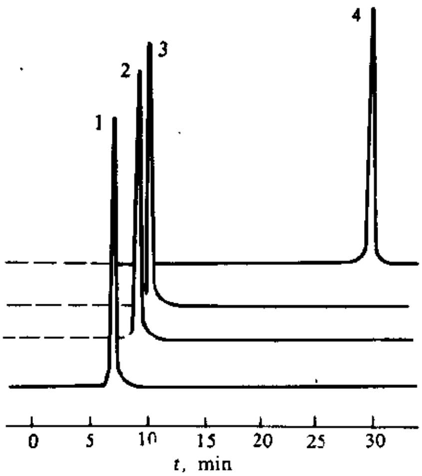


Fig. 6 HPLC chromatograms of standards
1: 2-chlorobenzamide 2: chlorobenzene
3: 4-chlorophenyl 4: CCU

The retention times of peak 1, 2, 3 and 4 in Fig. 5 are equal to those of 2-chlorobenzamide, chlorobenz ene, 4-chlorophenyl urea and CCU. They are 7.5, 9.3, 9.8 and 30.0 minutes, respectively. In order to verify these products, the UV absorption spectra of the photoproducts and the relative standards were compared with HP1090 HPLC (Fig. 7).

It can be seen from Fig. 7 that each pair of UV absorption spectra of the peak and of the standard are very similar. Thus, peak 1, 2, 3 and 4 in Fig. 5 are identified as 2-chlorobenzamide, chlorobenzene, 4-chlorophenyl urea and CCU.

2. Identification with GC-MS

The photoproducts were also identified through analyzing the mass spectra of the photoproducts taken from the GC-MS run, when nitrogen was used as saturating gas, the photoproducts include: isocyanato benzene, 4-chlorophenyl isocyanate, methylcaramate, 2-chlorobenzamide, N-(4-chlorophenyl) methylcarbamate and 2-chloro-N- (4-chlorophenyl) benzamide. The mass spectra of them are shown in Fig. 8. When oxygen was used as saturating gas, the photoproducts identified with GC-MS are almost the same to those with nitrogen as saturating gas, except with no isocyanato benzene.

Mechanism of photoreaction

The photoproducts of CCU in methanol identified with HPLC and GC-MS are summarized in Table 1.

Table 1 Possible photoproducts of CCU in methanol

Product	RT(HPLC), min	RT(GC-MS), min	Mol, wt	Main MS, fragm,	Formula
a	—	7.7	119	91	C_7H_5NO
b	—	13.8	153	155, 125, 90	C_7H_4ClNO
c	—	21.6	151	119, 92, 77	$C_8H_9NO_2$
d	7.5	26.2	155	157, 139, 111	C_7H_6ClNO
e	9.3	—	112	—	C_6H_5Cl
f	9.8	—	170	—	$C_7H_7ClN_2O$
g	—	28.4	185	187, 153, 126	$C_8H_8ClNO_2$
h	—	46.4	265	267, 139, 111	$C_{13}H_9Cl_2NO$

a. isocyanato benzene[2] *b*. 4-chlorophenyl isocyanate[2] *c*. N-phenyl methylcarbamate[2] *d*. 2-chlorobenzamide[1,2] *e*. chlorobenzene[1] *f*. 4-chlorophenyl urea[1] *g*. N-(4-chlorophenyl) methylcarbamate[2] *h*. 2-chloron-N-(4-chlorophenyl) benzamide[2] 1: Identifying method HPLC-UV 2: Identifying method GC-MS (tentative identification)

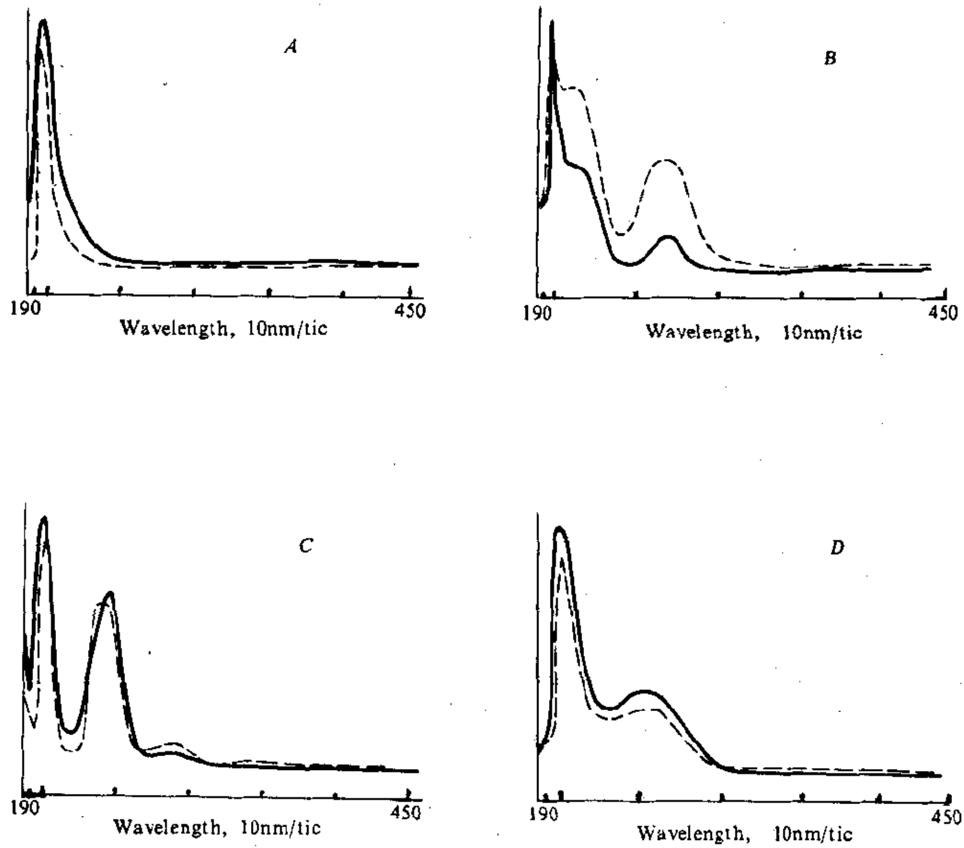


Fig. 7 UV absorption spectra of photoproducts in comparison with those of standards
(···photoproducts; – – –standards)
A: peak 1,2-chlorobenzamide; *B*: peak 2, chlorobanzene; *C*: peak 3,4-chlorophenyl urea *D*: peak 4, CCU

Through analyzing the photoproducts of CCU in methanol and the molecular structure of CCU, we propose the possible photoreaction pathways of CCU in methanol as follows (Rosen, 1969; Elad, 1965).

According to Walter (Walter, 1981), in the molecule of DFB the length of amide bond 1,2 and 3 are 1.410, 1.378 and 1.337 Å, respectively. That is to say bond 1 is the weakest and bond

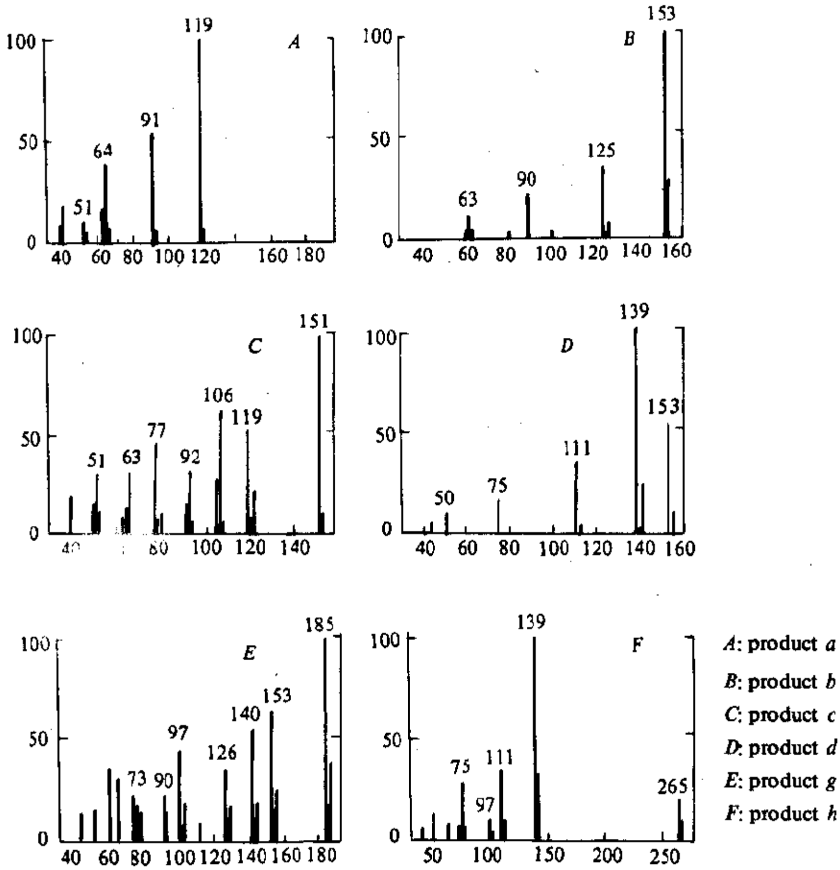
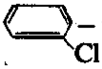
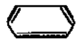
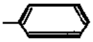
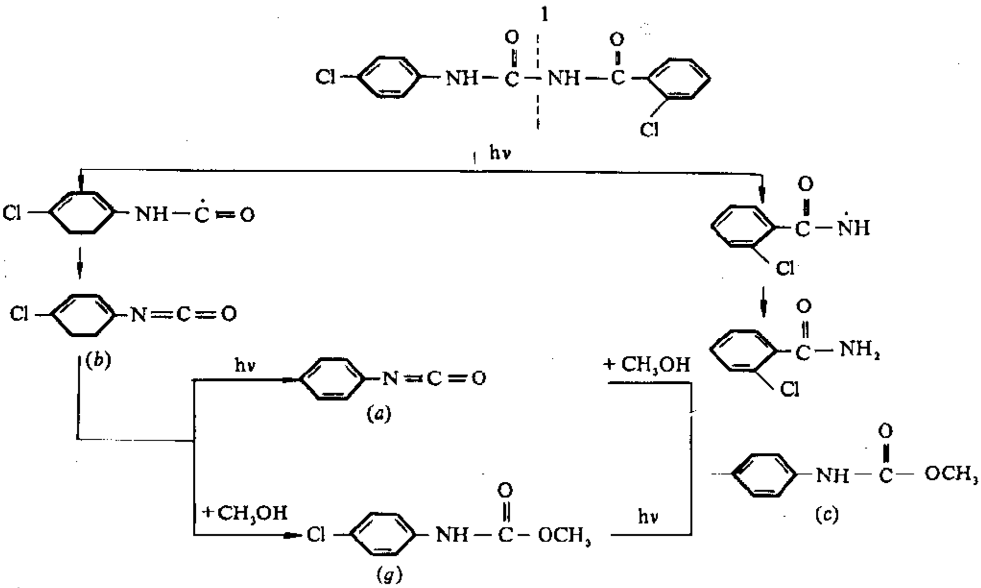


Fig. 8 Mass spectra of photoproduct

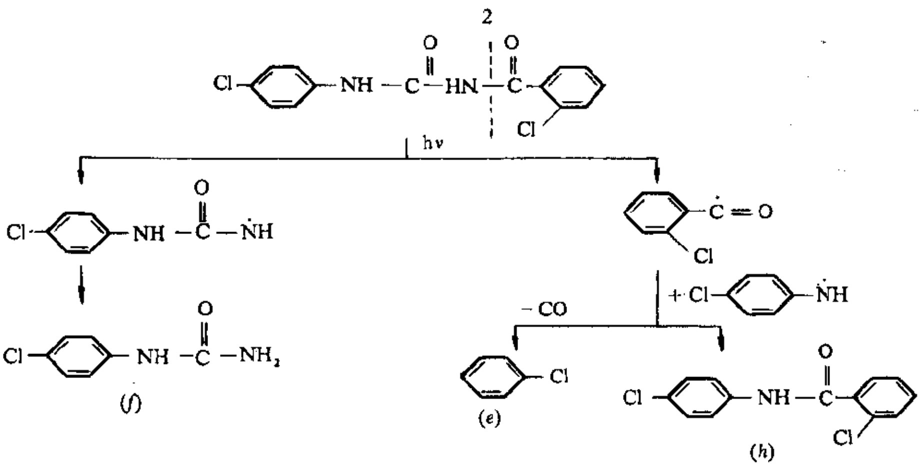
3 the most stable, while bond 2 is in median. The molecular structure of CCU is very similar to that of DFB. So bond 1 in CCU will be the easiest to break up, then will follow bond 2, and bond 3 the most difficult to break up. In pathway 1, bond 1 is broken up, so the photoproducts 2-chlorobenzamide and N-phenyl methylcarbamate that follow this pathway should be the main photoproducts. As bond 2 is easier to break up than bond 3, there might be more free radical

 $-\dot{C}=0$ than Cl–  –$\dot{N}$H, and thus  –Cl should be present in the photoproducts and Cl–  –NH_2 was not. All these are in consistent with the experimental results.

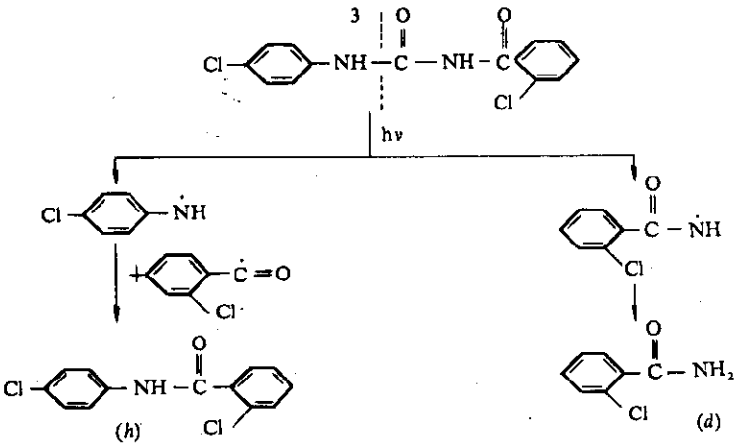
Pathway 1:



Pathway 2:



Pathway 3:



CONCLUSIONS

1. The photoreaction of CCU is easy to take place in methanol, and the reaction is of the first order. When nitrogen was used as saturating gas, the photoreaction rate constant was 0.118 h^{-1} and the half-life was 5.87 h. When oxygen was used as saturating gas, the photoreaction rate constant was 0.129 h^{-1} and the half-life 5.37 h. However statistically there is no significant difference between the two cases.

2. Under the experimental condition, the reaction rate is proportional to the light intensity, and the latter also has some effect on the relative concentration of the products, but none on the reaction order and the identities of products.

3. The main photoproducts of CCU in methanol identified by HPLC and GC/MS are: 2-chlorobenzamide, chlorobenzene and 4-chlorophenyl urea. Other possible photoproducts of CCU in methanol also include: N-phenyl methylcarbamate, N-(4-chlorophenyl) methylcarbamate, 2-chloro-N-(4-chlorophenyl) benzamide, 4-chlorophenyl isocyanate, and so on.

4. The photoreaction of CCU in methanol takes place through the breaking up of its amide bonds and methanol takes part in some reaction process.

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